A Manganese and Alkali Metal or Alkali Earth Metal Based Composite for NO$_x$ Trap and Its Application in Waste Gas Treatment

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[57] Abstract

This invention concerns a manganese and alkali metal or alkali earth metal based composite for NO_x trap and its application in waste gas treatment. The said composite contains carrier and active phase, whereas the active phase is based on manganese and at least another element A from alkali metal or alkali earth metal, and whereas manganese and element A are chemically bonded. The said composite can serve as NO_x trap in gas treatment in order to reduce the exhaustion of nitrogen oxide. The said gas is generated by internal combustion engine, especially diesel engine or dilute mixed gas engine.

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[1] Numbers in the margin indicate pagination in the foreign text.

Claims

What is claimed is:

1. A composite serving as NO_x trap and containing carrier and active phase, whereas the active phase is based on manganese and at least one other element A from alkali metal and alkali earth metal, and whereas manganese and element A are chemically bonded excluding the following situations: First, A is a potassium composite, where the carrier is cerium oxide and the two elements manganese and potassium are provided by potassium hypermanganate with atomic ratios of $[K]/([K]+[CeO_2])=0.16$ and $[Mn]/([Mn]+[CeO_2])=0.16$, respectively; Secondly, A is potassium composite, where the carrier is based on cerium oxide, zirconium oxide, and lanthanum oxide, where the weight ratio of oxide is 72/24/2, and where the carrier has 2.8ml oxygen/g oxygen storage capacity.

2. The composite in Claim 1, whereas the element A is potassium, sodium, or barium.

3. The composite in Claim 1 or Claim 2, whereas the carrier is based on the oxide from aluminum oxide, cerium oxide, zirconium oxide, or the mixture of cerium oxide and zirconium oxide.

4. The composite in Claim 3, whereas the carrier is based on cerium oxide and contains silicon oxide.

5. A method for preparing any one of the composites in the above claims, whereas the carrier is in contact with manganese and at least one other element A, or is in contact with the precursor of manganese and at least one other element A, and whereas the mixture is calcinated at the temperature high enough to form chemical bon between manganese and element A.

6. A gas treatment method for reducing the exhaustion of nitrogen oxide, whereas the method uses any one of the composites in Claims 1~4.

7. The method in Claim 6, whereas the method is employed for the treatment of waste gas exhausted form internal combustion engine.

8. The method in Claim 6, whereas the gas to be treated contains excessive oxygen relative to chemical measurement.

9. The method in Claim 7 or Claim 8, the oxygen content in the gas is at least 2% (volume).

10. A system for treating the waste gas exhausted from internal combustion engine, whereas the system contains any one of the composites in Claims 1~4.

11. The application of any one of the composites in Claims 1~4

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for manufacturing the system for the treatment of waste gas exhausted

from internal combustion engine.

Instructions

A Manganese and Alkali Metal or Alkali Earth Metal Based Composite for NO_x Trap and Its Application in Waste Gas Treatment

This invention concerns a manganese and alkali metal or alkali earth metal based composite for NO_x trap and its application in waste gas treatment. In practice, ternary catalytic cleaner is used to reduce nitrogen oxide (NO_x) in waste gas exhausted from automobile engines. The ternary catalytic cleaner makes use of the reducing gas in the mixed gases. However, excess oxygen will significantly deteriorate the catalyst performance.

Some engines such as diesel engines or dilute mixed gas and gasoline engines can effectively make use of thinners. However, they always exhaust waste gas containing substantial excess oxygen, such as at least 5% oxygen. In this situation, the standard ternary catalytic cleaner is ineffective in reducing the exhaustion of NO_x. In addition, more and more strict rules on vehicle engine combustion have been in place to restrict the exhaustion of NO_x.

To solve the above problem, various NO_x trap systems have been developed. These systems can oxidize NO into NO_2 and then absorb the

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generated NO_2. In some situations, NO_2 is leached out and reduced into

N_2 via the reducing substance contained in the waste gas. Nevertheless,

these NO_x traps have many shortcomings. For example, the optimal

operating range of these traps is in relatively low temperature area,

which is usually 200~270°C. At relatively high temperatures, the traps

are in low efficiency or ineffective. Therefore, it is important to

provide a system that is effective in higher temperatures than the

temperature range of the current systems. Furthermore, in water

thermal medium or high temperature oxidization medium, the trap

systems may present low thermal stability. Therefore, the improvement

on the thermal stability can be an advantage of the new trap system.

In addition, the existing trap systems usually use expensive metals,

which can be a problem in supply. In this sense, it is attractive

to develop non-expensive metal catalyst to reduce system cost.

Therefore, the objective of this invention is to provide a

composite that can be used as NO_x trap in high temperature, as well

as non-expensive metals in the composite. This invention also provides

an NO_x trap having good thermal stability.

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This invention concerns a composite serving as NO_x trap and

containing carrier and active phase, whereas the active phase is based

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on manganese and at least one other element A from alkali metal and alkali earth metal, and whereas manganese and element A are chemically bonded excluding the following situations: First, A is a potassium composite, where the carrier is cerium oxide and the two elements manganese and potassium are provided by potassium hypermanganate with atomic ratios of $[K]/([K]+[CeO_2])=0.16$ and $[Mn]/([Mn]+[CeO_2])=0.16$, respectively; Secondly, A is potassium composite, where the carrier is based on cerium oxide, zirconium oxide, and lanthanum oxide, where the weight ratio of oxide is 72/24/2, and where the carrier has 2.8ml oxygen/g oxygen storage capacity.

The other characteristics, details, and advantages of this invention are demonstrated through the following descriptions and non-restrictive implementations.

In the invention, the term "rare earth metal" refers to yttrium and No. 57~71 elements in periodic table of elements.

In the invention, the oxygen storage capacity is determined by the test that evaluates the amount of monoxide imported through continuous oxidization of carrier or product, or the amount of oxygen consumed in the importation of oxidized product. The test method is called substitution method.

The carrier gas is pure helium gas and the velocity of flow is

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10 L/h. The gas is imported by means of a circuit containing 16ml gas. CO is imported via mixed gas containing 5% CO diluted in helium, while O_2 is imported via mixed gas containing 2.5% O_2 diluted in helium. A thermal conductivity verification gas chromatograph is used for gas analysis.

The amount of consumed oxygen can be used to determine the capacity of oxygen storage. The characteristic value of oxygen storage capacity represents the product imported in milliliter oxygen (in normal temperature and pressure conditions) per gram, and is measured at 400°C. In the invention, the oxygen storage capacity is derived at 900°C in the air after pretreatment in muffle furnace for 6 hours.

The composite of this invention consists of carrier and active phase. The term "carrier" generally refers to the main element in the composite and/or having no catalytic activity or trap activity, or having the catalytic activity or trap activity different from that of active phase, or having other elements deposited on its surface. For simplicity purpose, the carrier and active phase or load phase are discussed in other sections of the invention. However, it should be understood that the scope of this invention also covers the situation where the said elements for forming active phase or load phase exist in the carrier and are imported in the carrier preparation

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process.

As a characteristic of the invention, the active phase is based

on manganese and at least one other element A coming from alkali metal

or alkali earth metal. The specific examples of alkali elements are

sodium and potassium. Barium can be used as an alkali earth metal

element. Since the composite may contain one or more kinds of elements

A, the description of element A in any part of this invention shall

be regarded as the description of several elements A.

In the composite of the invention, element manganese and element

A is chemically bonded, meaning that manganese and element A are linked

through chemical bond rather than in the form of simple mixture. For

example, element manganese and element A may exist in the form of

compound or mixed oxide phase. This compound or oxide phase can be

expressed with chemical formula $A_xMn_yO_{2-\delta}$ (1), where $0.5 \leq y/x \leq 6$ and the

value of δ has something to do with the nature of element A and the

oxidization state of manganese. The examples of the phase or compound

of chemical formula (1) include hydrated pyrolusite, basic isiganeite,

hybrid isiganeite or isiganeite, sodium manganite,

barium-magnesium-maganese ore, buserite, or potassiumphyllite

compound. The compound can be in hydrated or layered CdI_2 structure.

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In this invention, chemical formula (1) is provided for explanation purpose. The scope of this invention also covers compounds in different chemical formulas, provided that manganese and element A are chemically bonded. The X-ray analysis or electronic microscope analysis can prove the existence of such compound.

The oxidization state of manganese is in the range of 2~7, and specifically in the range of 3~7.

Element potassium and element manganese can exist in the form of $K_2Mn_4O_3$ compound. Barium can exist in the form of $BaMnO_3$ compound.

In this invention, the active phase basically consists of manganese and at least one other element A coming from alkali metal and alkali earth metal. Manganese and element A are chemically bonded. The so-called "basically consists of……" refers to the fact that the composite in this invention still has NO_x trap activity even in the absence of active phase of any element different from manganese and element A, such as expensive metal or other metal element for catalysis.

The composite in this invention also contains a carrier. The carrier can be any porous carrier for catalysis. Preferably, the carrier has enough chemical inertia to element manganese and element A in order to avoid obvious chemical reaction between one or more

elements and the carrier. Such chemical reaction may be harmful to the formation of chemical bond between manganese and element A. However, in the event of chemical reaction between the carrier and these elements, substantial amount of manganese and element A can be used in order to acquire the needed chemical bond between the elements.

The carrier can be any type of aluminum oxide carrier having the specific surface area high enough for catalysis. The examples of the carrier include at least one kind of aluminum hydrate coming from bayerite, gibbsite or hydrargillite, noyerite and/or at least one kind of aluminum hydroxide such as aluminum oxide formed by fast dehydration of boehmite, pseudoboehmite, or hard water bauxite.

Stable aluminum oxide can also be used as the carrier. The stabilizing element includes rare earth elements, barium, silicon, titanium and zirconium. The rare earth elements include cerium, lanthanum, or lanthanum-neodymium mixture.

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Stable aluminum oxide is traditionally prepared through impregnation of aluminum oxide with the salt of the above-mentioned stable elements such as nitrate solution, or through co-drying and calcinations of the precursor of aluminum oxide and the precursor

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of the salt of the above elements.

The carrier can also come from cerium oxide, zirconium or their mixtures.

The mixtures of above-mentioned cerium oxide and zirconium oxide are published in Europe Patent Applications EP-A-0605274 and EP-A-0735984, which are integrated into this invention. Specifically, it is possible to develop cerium oxide and zirconium based carrier, in which the cerium/zirconium atoms ratio of these oxides is at least 1. The carriers can also be in the form of solid solution. In this situation, the X-ray diffraction spectrum of the carrier has proved the existence of single homogeneous phase in the carrier. As for cerium-rich carrier, the phase corresponds to the phase of isometric crystalline cerium oxide CeO_2. However, the grid parameters are deviated from that of cerium oxide due to the adding of zirconium in the crystalline network of cerium oxide.

The carrier can also be the mixture of cerium oxide and zirconium oxide, as well as the mixture of rare earth mixture based on scandium oxide or different from cerium. The carrier especially refers to those disclosed in international patent applications WO97/43214, which are integrated into this invention. Specifically, the application discloses a cerium oxide, zirconium oxide and ytterbium oxide based

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composite, or the composite based on other oxides (except cerium) coming from at least scandium oxide and rare earth metal oxide. In this situation, the cerium/zirconium atom ratio is at least 1. After calcination at 900°C for 6 hours, the specific surface of the composite is at least 35m^2/g and the oxygen storage capacity at 400°C is at least 1.5ml oxygen/g.

In an implementation of the invention, the carrier is cerium oxide based and contains silicon oxide. Such carrier is disclosed in patent application EP-A-0207857 and EP-A-0547924, and this thus integrated into this invention.

The total content of manganese, alkali metal and alkali earth metal can be in a wide range. The minimum content refers to the content below which the NO_x absorption activity cannot be observed. This content can be in the range of 2~50%, and more specifically 5~30%. The content is expressed by the percentage (atom) % relative to the total moles of oxide in the carrier and elements involved in the active phase. The contents of manganese, alkali metal and alkali earth metal can be in a wide range. Specifically, the content of manganese can be equal or close to the content of alkali metal or alkali earth metal.

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In an interesting implementation of the invention, the alkali

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metal is potassium. The content (as calculated above) is 10~50% and preferably 30~50%.

The composite of the invention can be prepared by having the carrier to contact with manganese and at least one other element A, or with manganese or the precursor of at least one other element A, and calcinating the mixture at the temperature high enough to form chemical bond between manganese and element A.

One method for conducting the above contact is impregnation. Therefore, it is necessary to first prepare the salt or compound solution or slurry of load phase element. The salt may come from inorganic salt such as nitrate, sulfate or chloride, or organic salt, especially saturated fatty carboxylic salt or alkyl carboxylic salt. The examples of organic salt include formate, acetate, propionate, oxalate, and citrate. The dry impregnation method is employed to impregnate the carrier with the above solution or slurry. The dry impregnation method includes adding the element water solution equal to the volume of the impregnation hole to the impregnating product. It might be favorable to deposit active phase elements in two steps. For example, it is favorable to deposit manganese in the first step and deposit element A in the second step. After impregnation, the carrier is dried and calcinated. It should be pointed out that it

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is possible to use the carrier without calcination before impregnation. The active phase can also be deposited using the method of spray drying the salt or compound of the active phase element and the carrier's suspenoid.

As mentioned above, the invention does not include such composites in which the carrier is cerium oxide, the element A is potassium, the precursor of potassium and manganese in the above-discussed preparation method is potassium hypermanganate.

As mentioned above, the calcination is conducted at the temperature high enough to form chemical bond between manganese and element A. The calcinations temperature is related to the nature of element A. When the calcination is conducted in the air, the temperature is usually at least 600°C, preferably 700°C, and more preferably 800~850°C. When the chemical bond between manganese and element A has been formed, higher temperature is usually unnecessary. In addition, higher temperature may reduce the specific surface area of the carrier and further degrading the catalytic performance of the composite. The calcinations time is manly determined by temperature and is long enough to form chemical bond between the elements.

As mentioned above, the composite of this invention is in the

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form of powder. However, the composite can be in particle, small ball, cylinder, or cellular shape in any size.

This invention also concerns a method of applying the composite of the invention in gas treatment in order to reduce the exhaustion of nitrogen oxide. In the invention, the gas to be treated comes from gas combustion turbine, boilers in electricity generating station, or internal combustion engine. In the later situation, the engine can be diesel engine or dilute mixed gas engine.

The composite of this invention can be used as NO_x trap when it is in contact with high oxygen content gas. The term "high oxygen content gas" refers to the gas containing excess oxygen relative to the amount needed to fuel combustion in chemical measurement. More accurately, the gas contain excess oxygen relative to chemical measurement $\lambda=1$, or the gas with the value of λ greater than 1. The value λ is associated with the known air/fuel ratio. As far as internal combustion engine is concerned, the gas with excess oxygen may come from the gas of dilute mixed gas engine (e.g., the oxygen content in volume is at least 2%) and high oxygen content gas such as the gas from diesel engine. The oxygen content is at least 5%, or higher than 5%, or more specifically at least 10%. The range of the oxygen

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content can be within 5~20%.

This invention can also be applied for the above type of gases containing about 10% water in quantity.

This invention also involves in a gas treatment system for reducing the exhaustion of nitrogen oxide. The said gas is the type of gases mentioned above. More specifically, the gas refers to those containing excess oxygen relative to chemical measurement value. The system contains the above-mentioned composite. For example, it may contain the composite-based catalytic coating on the whole metal or ceramic substrate.

In the end, this invention also involves in the application of the composite in the production of such system.

This invention is further illustrated through the following implementations. In the implementations, the tests on NO_x trap assessment are conducted as follows: Place 0.15g particle-shape NO_x traps in a quartz reactor. The powders applied are firmly pressed, crushed, and then sieved to acquire 0.125~0.250mm granularity particles.

The reaction mixture at the entrance of the reactor contains the following components (in volume):

.NO: 300vpm

.O_2: 10%

.CO_2: 10%

.H_2O: 10%

.N_2:

The total velocity of flow is 30 standard liter/hour.

The HSV is about 150000 hour^{-1}.

The signals of NO and NO_x ($NO_x=NO+NO_2$) are recorded consecutively with the reactor temperature. NO and NO_x signals are generated by NOx ECOPHYSICS analyzer through chemical luminescence mechanism.

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The NO_x traps are assessed by measuring the NO_x quantity absorbed until the trap phase is saturated (trap or active phase expressed in mg NO/g). The experiment is repeated at different temperatures in 250~500°C range. With the experiment, it is possible to determine the optimum temperature zone where NO_x trap is effective.

Implementations 1~12

Raw Material

The raw materials include $Mn(NO_3)_24H_2O$, 99.5% potassium nitrate KNO_3; 99.5% barium nitrate $Ba(NO_3)_2$, and 99.5% sodium nitrate $NaNO_3$.

The carriers include HSA5® cerium oxide provided by Rhodia, HSA1® provided by Rhodia, zirconium oxide containing cerium oxide (ZrO_2/CeO_2

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weight ratio is 80/20) and HSA514[®] cerium oxide containing silicon oxide provided by Rhodia (99.15% CeO_2, 0/85% SiO_2). All carriers are calcinated at 500°C for 2 hours.

Composite Preparation

The active phase is based on manganese. Other element A is K, Ba or Na. The preparation steps are as follows:

Step 1: Deposition of the first load element

This step includes depositing 10% (atom) element Mn relative to the number of moles of the element and the number of moles of oxide in the carrier, i.e.:

$[Mn]/([Mn]+[oxide of carrier])=0.1$, i.e., [oxide of carrier]=0.9.

Step 2: Deposition of the second load element

This step includes depositing the second load element, which is 10% (atom) element relative to the number of moles of the oxide, i.e.:

$[A]/([Mn]+[A] + [oxide of carrier])=0.1$. In the formula, A=K, Ba, or Na.

In the dry carrier impregnation, it is necessary to consider the concentration of the load element to be dissolved in the solution with the volume equal to the volume of the carrier hole (0.5ml/g

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measured with water).

In this implementation, the elements are impregnated on the
carrier one by one through the following operating steps:

. Dry impregnate the first element;

. Dry up in the furnace (110°C, 2 hours);

. Calcinate at 500°C for 2 hours (5C/minute);

. Dry impregnate the second element;

. Dry up in the furnace (110°C, 2 hours).

After impregnation, calcinate the product in the air at 500°C,
600°C, 700°C, 800°C, and 850°C for 6 hours to obtain the following
composites:

For Implementations 1~8, HSA5[®] is used; For Implementations 9
and 10, HSA514[®] is used; For Implementation 11, ZrO_2/CeO_2 carrier is
used; For Implementation 12, HSA1[®] is used.

Control Implementation 1: [Mn]=10% (atom); [K]=10% (atom),
calcinate at 500°C for 2 hours. SBET=115m^2/g.

Implementation 2: [Mn]=10% (atom); [K]=10% (atom), calcinate
at 600°C for 2 hours. SBET=106m^2/g.

Implementation 3: [Mn]=10% (atom); [K]=10% (atom), calcinate
at 700°C for 2 hours. SBET=15m^2/g.

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Implementation 4: [Mn] =10% (atom); [K] =10% (atom), calcinate at 850°C for 6 hours. SBET=12m^2/g.

Implementation 5: [Mn] =10% (atom); [Ba] =10% (atom), calcinate at 500°C for 2 hours. SBET=112m^2/g.

Implementation 6: [Mn] =10% (atom); [Ba] =10% (atom), calcinate at 850°C for 6 hours. SBET=23m^2/g.

Implementation 7: [Mn] =10% (atom); [Na] =10% (atom), calcinate at 500°C for 2 hours. SBET=112m^2/g.

Implementation 8: [Mn] =10% (atom); [Na] =10% (atom), calcinate at 850°C for 6 hours. SBET=6m^2/g.

Implementation 9: [Mn] =10% (atom); [K] =10% (atom), calcinate at 800°C for 2 hours. SBET=6m^2/g.

Implementation 10: The composite is identical to that in Implementation 9, calcinate at 500°C for 2 hours. SBET=111m^2/g.

Implementation 11: [Mn] =10% (atom); [K] =10% (atom), calcinate at 850°C for 6 hours. SBET=11m^2/g.

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Implementation 12: [Mn] =10% (atom); [K] =10% (atom), calcinate at 850°C for 6 hours. SBET=5m^2/g.

SBET is specified as BET specific surface measured through nitrogen adsorption in conformity with standard ASTMD 3663-78 method.

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The above method is established according to BRVNAVER-EMMETT-TELLER

method as described in "Journal of America Society of Chemistry",

60, 309 (1938)".

In the control implementation, X-ray analysis shows the

existence of CeO_2 phase. In Implementations 2, 3, 4, 9, and 11, X-ray

analysis indicates the existence of both CeO_2 phase and $K_2Mn_4O_8$ phase,

as referred in JCPDS16-0205 search result. Microscope analysis shows

that Mn and K constitute about 200~300 nanometer large crystals. Mn

is in oxidization states III and IV. In Implementation 6, X-ray

analysis indicates the existence of CeO_2 phase and $Ba_{0.7}MnO_3$ phase.

In Implementation 8, X-ray analysis indicates the existence of CeO2

phase and $Na_{0.7}MnO_{2-\delta}$ phase.

The following tables list the result of NO_x traps in the

implementation products. The values in the tables correspond to NO_x

storage amount in the unit of mgNO/g active phase.

Table 1

T (°C)	Implementation					
	1	2	3	4	5	6
250	12.4	8.5	5.8		7.4	
300	10.8	13.5	12.9	1.2	5.5	3.6
350	7.1	12.4	12.3	10.2	0.7	4.1
400	2.4	9.5	11.1	9.1	0	1.7
450	0	6.4	8.5	7.4		1.3
500		3.6		6.6		

Table 2

T (°C)	Implementation					
	7	8	9	10	11	12
250	8.9					
300	7.8	1.2	1.6	12.2	6	1.7
350	3.1	3.0	5.9	10.5	13.7	10.6
400	0	3.0	7.4	8.3	11.1	9.3
450		1.0	7.5	4.4	10.7	7
500			5.9	0.6	7.6	6.4

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Compared with Manganese and other elements without chemical bonding, the composite in the invention shows that $T_{maximum}$ has large displacement towards high temperature. Furthermore, the composite is also effective in NO_x storage even without containing platinum or other expensive metals.

Implementation 13

This implementation demonstrates the thermal stability of the composite in the invention.

Use the composite described in Implementation 4. Calcinate the composite in nitrogen atmosphere containing 10% (volume) hydrogen at 750°C for 6 hours. The catalytic result of the composite is shown in the following table. For comparison purpose, the result of Implementation 14 is also listed in the table.

Table 3

T (°C)	Implementation 13	Implementation 14
250		
300	2.3	1.2
350	10.4	10.2

400	9.3	9.1
450	6.9	7.4
500	5.4	6.6

No clear difference between the results of aged products in Implementation 13 and Implementation 4 is observed.

Implementation 14

In this implementation, the cerium oxide, zirconium oxide, and lanthanum oxide based carrier is employed. The $CeO_2/ZrO_2/La_2O_3$ weight ratio is 67/23/10. The carrier is calcinated at 800°C for 2 hours.

Under the above conditions, dry impregnation is conducted using manganese and potassium in the following mole ratios:

$[Mn]/([Mn] + [carrier\ oxide]) = 0.1$

$[K]/([K] + [Mn] + [carrier\ oxide]) = 0.4$

After impregnation, calcinate the product at 850°C for 2 hours. The SBET is $2m^2/g$.

The NO_x storage amount is given in the following Table 4:

Table 4

Temperature	NO_x Amount
300°C	3.9
350°C	11.5
400°C	20.7
450°C	34.3

In this implementation, extremely high NO_x storage amount is

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observed.

<u>Implementation 15</u>

In this implementation, the aluminum oxide based carrier is employed. The carrier is calcinated at 500°C for 2 hours. Under the above conditions, dry impregnation is conducted using manganese and potassium in the following mole ratios:

$[Mn]/([Mn] + [Al_2O_3])=0.1$

$[K]/([K] + [Mn] + [Al_2O_3])=0.2$

After impregnation, calcinate the product at 750°C for 6 hours. The SBET is $2m^2/g$.

The NO_x storage amount is given in the following Table 5:

Table 5

Temperature	NO_x Amount
300°C	23.3
350°C	(*not legible*)
400°C	18.8
450°C	12.5